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Spectroscopic Characterization of the Water Oxidation Intermediates in the Ru-based Catalysts for Artificial Photosynthesis

Dooshaye Moonshiram[1], Igor Alperovich[2], Johna W. Jurss[3], Javier Concepcion[3], Thomas Meyer[3], and Yulia Pushkar[1]

[1]Department of Physics, Purdue University, 525 Northwestern Avenue, West Lafayette, IN 479071
[2]Research Center for Nanoscale structure of Matter, Southern Federal University, 5 Sorge St., 344090 Rostov-on-Don,
Russian Federation
[3]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599

Utilization of sunlight requires solar capture, light-to-energy conversion, and storage. One effective way to store energy is to convert it into chemical energy by fuel-forming reactions such as water splitting into hydrogen and oxygen. Ruthenium (Ru) complexes are among few molecular-defined catalysts capable of water splitting. Insight into the mechanism of their action will help to design future robust and economically feasible catalysts for light-to-energy conversion.

We characterized structures and electronic configurations of intermediates of water oxidation by "blue dimer" *cis,cis*-$[Ru_2O_3(H_2O)_2(bpy)_4](PF_6)_4$ and recently discovered monomeric Ru-complexes [1]. Intermediates of water oxidation were prepared chemically by oxidation of Ru-complexes with defined number of Ce(IV) equivalents and freeze-quenched at controlled times. Changes in the oxidation state of the Ru atom were detected by x-ray absorption near-edge structure at Ru $L_{2,3}$- and K-edges. We demonstrate that both L and K-edges are very sensitive to changes in Ru oxidation state for Ru(II), (III), (IV) and (V) complexes and thus allow a clear assignment of Ru oxidation state in intermediates. Extended x-ray absorption fine structure at Ru K-edge demonstrated structural changes in intermediates. We detected considerable changes in distances for Ru-N and Ru-O interactions as well as changes in the angle of Ru-O-Ru fragment in "blue dimer" molecule.

1. J. J. Concepcion, J. W. Jurss, J. L. Templeton, and T. J. Meyer, "One Site is Enough. Catalytic Water Oxidation by $[Ru(tpy)(bpm)(OH_2)]^{2+}$ and $[Ru(tpy)(bpz)(OH_2)]^{2+}$," *Journal of American Chemical Society*, **49**, 130, 16462–16463, (2008).